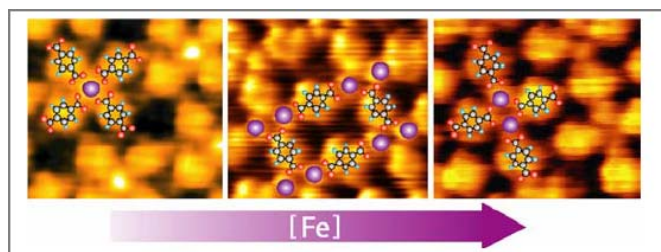
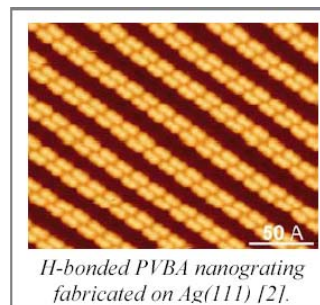


Molecular Engineering at Surfaces

J.V. Barth

Institut de Physique des Nanostructures, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland, and Advanced Materials and Process Engineering Laboratory, University of British Columbia, Vancouver, BC V6T 1Z4, Canada.

Pathways towards the engineering of low-dimensional supramolecular nanosystems at surfaces are expounded. We work towards nanoscale control and fabrication of distinct functional aggregates stabilized by non-covalent bonds (H-bonding, metal-ligand interactions) using adequate (self-)assembly protocols [1]. Upon depositing molecular building blocks at well-defined templates the nature and organization principles of supramolecular nanosystems can be comprehensively elucidated. Temperature-controlled scanning tunneling microscopy observations are presented providing atomistic insight into the underlying surface bonding and lateral coupling of functional species. In particular, polytopic carboxylic acids at metal surfaces were employed (e.g., 4-*[trans-2-(pyrid-4-yl-vinyl)]-benzoic acid (PVBA)*, 1,3,5-benzenetricarboxylic acid (TMA), 1,4-benzenedicarboxylic acid, etc.). With systematic investigations we addressed the sensitive balance of intermolecular and molecule-substrate interactions. By choosing the apt substrate material and symmetry the construction of distinct supramolecular nanostructures was achieved. On Ag(111) we synthesized one-dimensional nanogratings of supramolecular chiral H-bonded PVBA twin chains [2] and H-bonded open honeycomb networks from TMA. The formation and dynamics of coordination compounds with TMA and metal adatoms could be followed on Cu(001) at the single molecule level [3]. Furthermore nanoporous metallosupramolecular networks with specific topologies and a high structural stability have been fabricated by sequential deposition of polytopic carboxylate linker molecules and transition metal centers [4]. Their rational design and functionalization allows for the steering of molecular organisation and host-guest interactions. The accommodation of C₆₀ *H-bonded PVBA nanograting fabricated on Ag(111)* [2]. guest molecules is used to demonstrate the nanoarrays' aptitude as versatile and robust templates for the handling of nanoscale objects [5].



Modular assembly of metallosupramolecular architectures from Fe atoms and 1,4-benzenedicarboxylate linkers. Topology and stoichiometry are controlled by constituent concentration and annealing parameters. Fe atoms highlighted as pink spheres [6].

References:

- [1] J.V. Barth, J. Weckesser, N. Lin, A. Dmitriev and K. Kern, *Appl. Phys. A* **76**, 645 (2003).
- [2] J.V. Barth, J. Weckesser, G. Trimarchi, M. Vladimirova, A. De Vita, C. Cai, H. Brune, P. Günter and K. Kern, *J. Am. Chem. Soc.* **124**, 7991 - 8000 (2002).
- [3] N. Lin, A. Dmitriev, J. Weckesser, J.V. Barth and K. Kern, *Angew. Chem. Int. Ed.* **41**, 4779 (2002); *J. Am. Chem. Soc.* **124**, 14000 (2002).
- [4] A. Dmitriev, H. Spillmann, N. Lin, J.V. Barth and K. Kern, *Angew. Chem. Int. Ed.* **42**, 2670 (2003); *J. Am. Chem. Soc.* **125**, 10725 (2003).
- [5] S. Stepanow, M. Lingenfelder, A. Dmitriev, H. Spillmann, N. Lin, Ch. Cai, J.V. Barth and K. Kern, *Nature Mat.* in print (2004).
- [6] M. Lingenfelder, H. Spillmann, A. Dmitriev, S. Stepanow, N. Lin, J.V. Barth and K. Kern, *Chem. Eur. J.*, in print (2004).